



Unprecedented high photocatalytic activity of nanocrystalline WO₃/NiWO₄ hetero-junction towards dye degradation: Effect of template and synthesis conditions

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ABSTRACT

Nanocrystalline NiWO₄ wolframite structure has been prepared by a simple salt solution addition (NiW_{1SS}), co-precipitation (NiW_{4COP}) and sol-gel (NiW_{4SG}) techniques via employing polymeric templates particularly polyethylene glycol (PEG) and triblock copolymer, respectively. The synthesis method as well as the metal molar ratio (W/Ni) influenced the phases, morphology, optical and surface properties of synthesized samples as configured by X-ray diffraction, transmission electron microscopy, UV–vis diffuse reflectance spectroscopy, infrared spectroscopy, X-ray photoelectron spectroscopy and N₂ sorption techniques. Accordingly, the NiW_{1SS} material that exposed only NiWO₄ of nano-plate shape at a molar ratio (W/Ni) 1 indicates higher surface texturing values ($S_{\text{BET}} = 52.6 \text{ m}^2/\text{g}$, $V_p = 0.2061 \text{ cm}^3/\text{g}$ and $r = 15.7 \text{ nm}$) exceeding those of NiW_{4COP} ($S_{\text{BET}} = 15.07 \text{ m}^2/\text{g}$, $V_p = 0.0491 \text{ cm}^3/\text{g}$ and $r = 13.0 \text{ nm}$) of anisotropic shapes (hexagonal and tetragonal); synthesized at a ratio of 4 and by the same template (PEG). The NiW_{1SS} material indicated E_g value of 2.23 eV whereas that of NiW_{4COP} revealed a value of 2.92 eV. On the other hand, NiW_{4SG} that exposed well crystallized WO₃ beside NiWO₄ of nano-flakes shape and an average diameter of 25 nm indicates E_g value of 2.56 eV and in addition evokes the formation of narrow pore size distribution in mesopores range (2–12 nm) as well as in macropores (60 nm) exploring the effect of template type on the pore texturing. Photodegradation of methylene blue (MB) dye was used to evaluate the photoactivity of NiWO₄ catalysts under UV irradiations. The NiW_{4SG} catalyst exhibited the best degradation performance (92.5% for MB after 5 h). The results showed that the feasibility of MB degradation was not only due to morphological properties but also to the NiWO₄/WO₃ heterojunction. Significantly, WO₃ facilitates effective charge separation as traced by the photoluminescence emission spectra.

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1. Introduction

Transition metal tungstates have many applications, such as in gas sensors, optical fibres, humidity sensors, pigments and catalytic reactions [1–5]. Among these tungstates, nickel tungstate (NiWO₄) has been extensively studied. Mixed nickel–tungsten oxide, denoted as NiWO₄, may have properties that are superior to those of the two components. NiWO₄ has important electrochromic properties, besides a high long-lasting structural stability [6] and good catalytic properties [7]. The later tungstate crystallizes with wolframite structure that has monoclinic unit cell and space group P2/c characterized by alternating layers of nickel and tungsten atoms parallel to the (100) plane [8]. The coordination around

tungsten and nickel atoms is six, giving ribbons of like-filled octahedra sharing edges but unlike octahedra share corners [9]. In this way W₂O₈ structural units are formed in NiWO₄ similar to those of the CdWO₄ compound [10]. Usually single crystalline NiWO₄ can be prepared by solid state synthesis at high temperature [11,12] by co-precipitation from aqueous solutions of soluble salts [13,7] and by microwave assisted synthesis [14]. Several methods of chemical synthesis, on the other hand, have gained popularity for preparation of ceramic oxides including tungstates such as sol-gel, hydrothermal, citrate gel, polymeric precursors and gel combustion [15,16]. Chemical and physical properties of metal oxides and in particular tungstates are generally dependent on the synthesis route. Although transition metal tungstates have sufficient chemical and thermal stability [17,18] very few reports are available in the literature regarding their uses as photocatalysts for environmental remediation. Recently, the appreciable activity of ZnWO₄ for the degradation of Rhodamine B was

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reported [19–21]. Enhancement of the photocatalytic activity of ZnWO_4 doped with fluoride ions was also observed but never exceeds 10% [22]. Accordingly, the main objective is to elucidate the structural evolution of the phases that emerge when an atomic ratio of W/Ni equals 4 via employing polymeric precursors including triblock copolymer and polyethylene glycol. This is intentionally performed to see to what extent the presence of WO_3 will affect the structure, morphology as well as the photocatalytic performances of NiWO_4 . Sol–gel, co-precipitation and facile salt solution addition techniques were successfully used in the synthesis of nickel tungstate nanoparticles of controlled morphologies. Hence, the present work is aimed at studying the phases, morphology, optical, surface properties and structural transformations of the produced NiWO_4 compound using X-ray diffractometry (XRD), TEM, X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy, photoluminescence, and FTIR spectroscopy beside surface texturing properties (N_2 adsorption). In addition, the photoactivity of as-synthesized nanoparticles will be tested for the degradation of methylene blue (MB) dye.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation of NiWO_4 by an atomic ratio (W/Ni) of 1 using simple addition method

Analytical-grade nickel nitrate and sodium tungstate were used as received from Merck Company. The NiWO_4 was formed by precipitating a stoichiometric mixture of sodium tungstate and nickel nitrate solutions according to the following procedure. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (32.9 g) dissolved in 100 ml of distilled water containing polyethylene glycol-2000 $[(\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H})\text{-PEG 2000-2 g/100 ml water}]$ was poured on $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in PEG (29.0 g/100 ml water PEG). Following addition, a green precipitation was formed while vigorous stirring. The precipitate was left for one day, filtered, and washed with distilled water for several times. Then, dried at 110°C for 5 h and finally calcined at 400°C for 6 h to obtain NiWO_4 . This sample was denoted as $\text{NiW}_{1\text{SS}}$ where 1 corresponds to a W/Ni atomic ratio of 1 where SS represents salt solution by which the catalyst was simply synthesized.

2.1.2. Preparation of NiWO_4 by an atomic ratio (W/Ni) of 4 using co-precipitation method

Ni was first dissolved in water containing PEG-2000 (100 ml) and same for Na_2WO_4 . The later solution was poured onto the former under vigorous stirring to produce a blue suspension. Ammonia solution (15%) was then added into the suspension in a drop wise manner until complete precipitation followed by heating at 85°C for 6 h. The blue suspension was changed into green precipitate which filtered, washed with excess water and dried at 110°C for 10 h. Calcinations at 400°C for 6 h were accomplished. This sample was denoted as $\text{NiW}_{4\text{Cop}}$, where 4 accounts for the atomic ratio of 4/1 (W/Ni) and Cop accounts for the used method co-precipitation.

2.1.3. Preparation of NiWO_4 by an atomic ratio (W/Ni) of 4 using sol–gel method

Appropriate amounts of Na_2WO_3 and $\text{Ni}(\text{NO}_3)_2$ were used so as to obtain a 4:1 atomic ratio in the final product. Sodium tungstate was first dissolved in triblock copolymer-pluronic 123 [consisting of (ethylene oxide)₂₀ (propylene oxide)₇₀ (ethylene oxide)₂₀] – solution (1 g/100 ml)] followed by pH adjustment to a value of 8.8 via drop-wise addition of ammonia solution (15%, v/v). On the other hand, the solution of nickel nitrate dissolved also in

the triblock copolymer (1 g/100 ml) was added to that of the latter and thus the reacting solutions were kept at 60°C under vigorous stirring until a gel was formed. After gelation for 24 h in Teflon lined autoclave at the same temperature (60°C), the gel was dried at 110°C over night then calcined at 400°C for 6 h. This sample was denoted as $\text{NiW}_{4\text{SG}}$ where SG is accounted for the sol–gel method of preparation.

2.2. Catalyst characterization

2.2.1. X-ray diffraction analysis

X-ray diffraction analysis was performed on X-ray diffractometer (XRD) Model XRD 8030 from Jeol Co., Japan. Maximum power is 3 kW and the unit is equipped with rotating stage and thin layer accessories. The patterns were run with co-filtered $\text{CoK}\alpha$ radiation ($\lambda = 1.79 \text{ \AA}$) energized at 45 kV, and 10 mA. The samples were measured at room temperature in the range of $2\theta = 10\text{--}80^\circ$. The XRD phases present in the samples were identified with the help of ASTM Powder Data Files.

2.2.2. Transmission electron microscopy (TEM)

The nanostructured morphologies of the samples were examined using high resolution transmission electron microscopy (HRTEM) obtained by Tecnai G2 super twin USA, with an accelerating voltage of 200 kV. The elemental composition of the composite material was investigated by energy-dispersive X-ray attached to the TEM equipment. The average particle diameter (d) was calculated by the following formula: $d = \sum n_i d_i / \sum n_i$, where n_i is the number of particle diameter d_i in a certain range, and $\sum n_i$ is more than 200 NiWO_4 particles on TEM images of the sample. Computer-assisted counting of nanoparticle images and automated image analysis based software package including KONTRON KS 400 (Zeiss-Kontron) was used. To show how much variation from the average the calculated standard deviation of all nanoparticle sizes is stated in the text of this paper.

2.2.3. Fourier transform infrared spectra (FT-IR)

The infrared spectra of the samples were recorded in the range of $400\text{--}1000 \text{ cm}^{-1}$. The method includes mixing few milligram of a fine powder of the sample with KBr powder in an agate mortar. The mixture was then pressed by means of hydraulic press. The transmission was automatically registered against wavenumber (cm^{-1}) using a Perkin-Elmer instrument (Spectrum GX), made in USA.

2.2.4. Nitrogen adsorption measurements

Nitrogen adsorption measurements were performed at liquid nitrogen temperature with a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to the measurements, the samples were degassed for half an hour at 363 K followed by 3 h at 473 K. Surface area was calculated using the BET (Brunauer–Emmett–Teller) interpretation of the nitrogen adsorption isotherm.

2.2.5. UV–vis diffuse reflectance spectroscopy

Diffuse reflectance UV–vis spectroscopy (UV–vis DRS) of powder samples was carried out at room temperature using a PerkinElmer Lambda-900 spectrophotometer in the range of 200–800 nm. The UV–vis spectra were processed with Microsoft Excel software, consisting of calculation of the Kubelka–Munk function, $F(R_\infty)$, which was extracted from the UV–vis DRS absorbance. The edge energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of the plot of $[F(R_\infty)h\nu]^2$, for the direct allowed transition, vs. $h\nu$, where $h\nu$ is the incident photon energy.

2.2.6. Photoluminescence spectroscopy

The PL spectra were recorded by photoluminescence (PL) spectrometer (Spectro Fluorescence JASCO fp-6200) using 290 nm as excitation wavelength at room temperature via pulsed YAG:Nd laser excitation.

2.2.7. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were taken on the Thermo Scientific Escalab 250Xi spectrometer equipped with an MCD-9 detector and XR6 monochromatic source. This offers a user-selectable spot size from 200 to 900 μm . Automated in-lens irises may also be used to reduce the analysis area, offering a range of 300–20 μm . Spectra treatment were performed using the CASA software. The dual ion/electron flood source charge neutralization system, using very low energy electrons and ions, was used for the analysis of insulating samples. Typically the hydrocarbon C 1s line at 284.8 eV was used for energy referencing. All data processing (quantification, peak fitting, image generation, PCA, average spectrum generation, etc.) was performed within the Avantage data-system.

2.3. Photocatalytic activity

The photocatalytic properties of the various samples were evaluated by monitoring the degradation of methylene blue (MB, 350 ml, 20 ppm) dye in the presence of 200 mg of catalyst at room temperature. TiO_2 (P25, 20% rutile and 80% anatase) purchased from ACROS was tested as well for comparison purposes. All photodegradation experiments were performed in two side arms quartz photochemical reactor fitted with a cooling jacket. 125 W UV high pressure mercury lamp transmitted light in the wavelength range of 295–390 nm fitted with long Teflon tube was inserted into the reaction solution. Prior to irradiation, the catalyst and methylene blue solution were allowed to stir in the dark for 30 min prior to illumination to allow for adsorption of the methylene blue onto the surface of the catalyst. Aliquots of the solution were collected at different time intervals for a total of 400 min. The centrifuged aliquots were directed to UV–vis spectrophotometer to check the degradation of methylene blue dye via its absorption peak at 665 nm. This absorption data was used in the determination of degradation of the dye through comparison with the absorbance at a certain time as a percentage of the initial absorbance.

3. Results and discussion

3.1. XRD and TEM investigations

The XRD patterns of calcined samples are shown in Fig. 1. The pattern of NiW_4Cop indicates the main diffraction peaks of monoclinic NiWO_4 phase at $2\theta = 65.9^\circ, 54.7^\circ, 52.4^\circ, 49^\circ, 41.8^\circ, 36.6^\circ, 31.0^\circ, 25.0^\circ$, and 24.0° [JCPDS: 15-0755] which correspond to the (3 1 1), (2 0 2), (1 3 0), (0 0 2), (1 0 2), (2 0 0), (1 1 1), (1 1 0) and (0 1 1) crystallographic planes, respectively. Very small lines at $2\theta = 16^\circ, 17^\circ, 28^\circ$ and 33.2° have also been included and ascribed to WO_3 of low crystallinity [23]. The XRD pattern of $\text{NiW}_{1\text{SS}}$ reveals diffraction peaks typical to those of NiWO_4 seen in NiW_4Cop . Diffractions of the later indicate much lower crystallinity than that of the former suggesting a decrease in crystallites size of NiWO_4 in NiW_4Cop comparatively. In conformity, the particles size assessed using Scherrer equation based on using the (1 1 1) reflection at 31.0° were found to be 42 and 48 nm for NiW_4Cop and $\text{NiW}_{1\text{SS}}$, respectively (Table 1). This indeed indicates that the NiWO_4 formed by the simple method at an atomic ratio of (W/Ni) 1 initiates nearly pure monoclinic NiWO_4 phase with negligible amount of low crystalline WO_3 phase [23] unlike the case in NiW_4Cop . The $\text{NiW}_{4\text{SG}}$ sample shows typical diffraction peaks of monoclinic NiWO_4 phase of lower intensities than that

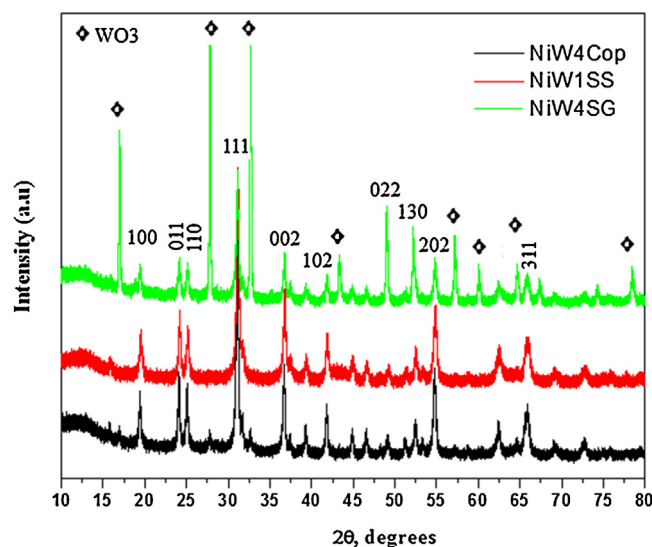


Fig. 1. XRD patterns of $\text{NiW}_{1\text{SS}}$, $\text{NiW}_{4\text{SG}}$ and $\text{NiW}_{4\text{Cop}}$.

in $\text{NiW}_{1\text{SS}}$, and thus indicates particles size comprised of 35 nm. Very strong peaks at $2\theta = 28.2^\circ, 32.8^\circ, 43.5^\circ, 57^\circ, 60^\circ, 64.8^\circ$ and 78.7° were also depicted in this sample, characterizing highly crystalline WO_3 phase (JCPDS card 43-1035). This reflects the role played by the polymer template in growing one phase while retarding the other. An exhibited strong interaction between W ions and PEG in NiW_4Cop is attained; and hence low crystalline WO_3 is emerged together with the highly crystallized NiWO_4 phase. On the contrary, promotion of NiWO_4 formation in $\text{NiW}_{4\text{SG}}$ with low crystallinity together with well crystallized WO_3 phase admits that a quite weak interaction between W ions and the triblock copolymer template is proposed. Accordingly, the tendency of the template to interact with the excess of W ions in the nominal molar ratio of 4 (W/Ni) affects the phases produced (NiWO_4 and WO_3) as well as their percentages in NiW_4Cop and $\text{NiW}_{4\text{SG}}$.

The morphologies of NiWO_4 samples were examined by TEM. The TEM image of $\text{NiW}_{1\text{SS}}$ shown in Fig. 2a revealed a nanoplates-like structure with an average size of 40 ± 3 nm. The inset in the figure illustrates the SAED pattern of NiWO_4 nanocrystals that perfectly indexed to a monoclinic wolframite structure, via the existed facets at (1 1 1), (2 0 0) and (3 1 1) [24]. This was in good agreement with the XRD results. The pattern of $\text{NiW}_{1\text{SS}}$ shows rings, characteristic of nanocrystalline materials, with some scattered ones. The EDS spectrum, with elemental analysis, of this sample indicates (not shown) 50% of C, 33.6% of O, 8.3% of Ni and 8.1% of W on the surface. The ratio of W/Ni is stoichiometrically equal 1 as planned during the synthesis process.

The TEM image of NiW_4Cop exhibits anisotropic shapes of hexagonal and tetragonal nanoplates with an average diameter of 34 ± 2 nm and length of 25–55 nm. The corresponding SAED pattern of the sample, shown as inset in Fig. 2b, indicates diffraction rings ascribed to (1 1 1), (2 0 0) and (3 1 1) of NiWO_4 crystalline phase. The corresponding EDS spectrum of the sample indicates (not shown) 36.5% of C, 20.1% of O, 4.6% of Ni, 19.9% of Cu and 18.8% of W. The content of Ni and W was near to the nominal value of 1:4 as intentionally suggested during the preparation. The presence of Cu was due to the copper grid used in the TEM measurements. Although the percentages of C is lower than that in $\text{NiW}_{1\text{SS}}$ we cannot neglect the carbon impurities derived from the non-complete decomposition of the PEG template that has been ascertained using the TG technique (not shown).

Table 1
Surface texturing, particles size and phases of synthesized NiWO₄ catalysts.

Sample name	S_{BET} (m ² /g) ^a	V_p (cm ³ /g) ^b	r (nm) ^c	Particle size (nm) ^d	Composed phases ^e
NiW _{1SS}	52.6	0.2061	15.7	48	mNiWO ₄ + nLcWO ₃
NiW _{4Cop}	15.1	0.0491	13.2	42	mNiWO ₄ + LcWO ₃
NiW _{4SG}	4.7	0.0164	13.9	35	mNiWO ₄ + HcWO ₃

^a S_{BET} , BET surface area.
^b V_p , pore volume.
^c r , BJH adsorption average pore diameter.
^d Crystallite sizes determined by the broadening of the NiWO₄ (1 1 1) facet diffraction peak using the Scherrer formula.
^e Composed phases where m denoted for monoclinic, nLc for negligible amount of low crystalline, Hc for high crystalline and Lc for low crystalline.

The TEM image of NiW_{4SG} shows irregular crystalline nano-flakes structure with average sizes of 25 ± 2 nm. The HRTEM-inset in this figure shows distances at 2.0 Å and 1.49 Å, which correspond to (2 2 2) and (1 1 1) planes of WO₃ and NiWO₄ phases, respectively. This signifies the close proximity of the two phases. This close interconnection between the two phases is supposed to favour the photoinduced electrons transfer between the phases that assume to reduce the recombination of the photoinduced electrons and holes, and improve the photocatalytic activity of the catalysts. The corresponding EDS pattern of the sample indicates that the elemental composition of W/Ni ratio was lower than 4 proposing that W was not exposed on the surface. Decreasing the particle size of this sample comparatively explains the role of triblock copolymer template in slowing the nucleation rate via the sol–gel technique however resulted in non-homogeneous nucleation so as to producing such irregular flaky structure.

3.2. Surface texturing properties

Fig. 3 shows the N₂ adsorption–desorption isotherms of the mixed oxide composites calcined at 400 °C. They belong to type II according to the IUPAC classification. The non-limiting adsorption at high P/P^0 is characteristic of Type H3 loop. The BET analysis revealed that the NiW_{1SS} sample exhibits higher surface area of 52.6 m²/g exceeding 15.07 m²/g of NiW_{4Cop} and 4.7 m²/g of NiW_{4SG} (Table 1). It has been reported that both pure NiO and WO₃ exhibit low surface area (4 and 9 m²/g, respectively) values [25,26]. Accordingly, the enhancement in surface area particularly in NiW_{1SS} is likely due to the presence of the PEG template that hinder the crystallization of NiO and WO₃ preventing the formation of large particles. The pore-size distribution obtained for NiW_{1SS} acquired from N₂ adsorption indicates that it's composed of mesoporous distribution centred at 250 Å. The pore size distribution obtained for

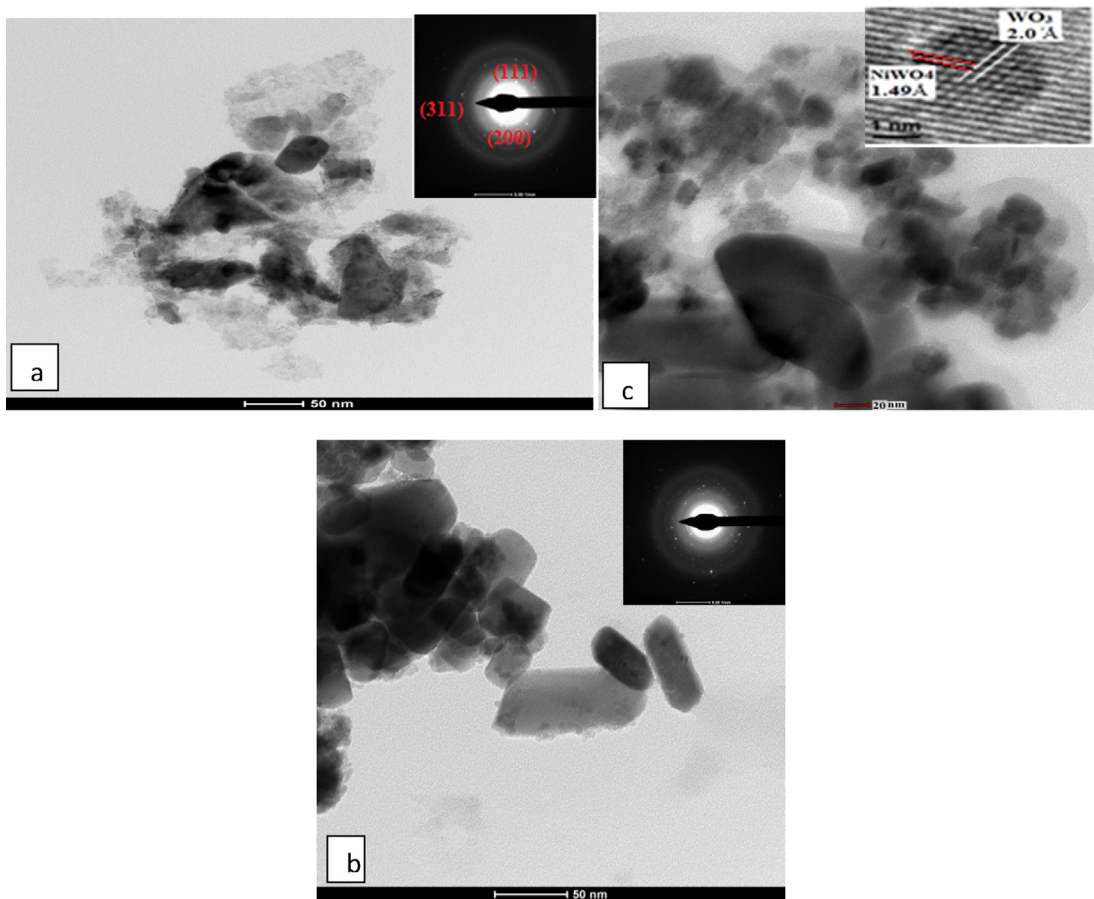


Fig. 2. TEM image of (a) NiW_{1SS}; (b) TEM image of NiW_{4Cop}, the inset in (a) and (b) shows the corresponding SAED patterns; (c) TEM image of NiW_{4SG} with HRTEM inset figure.

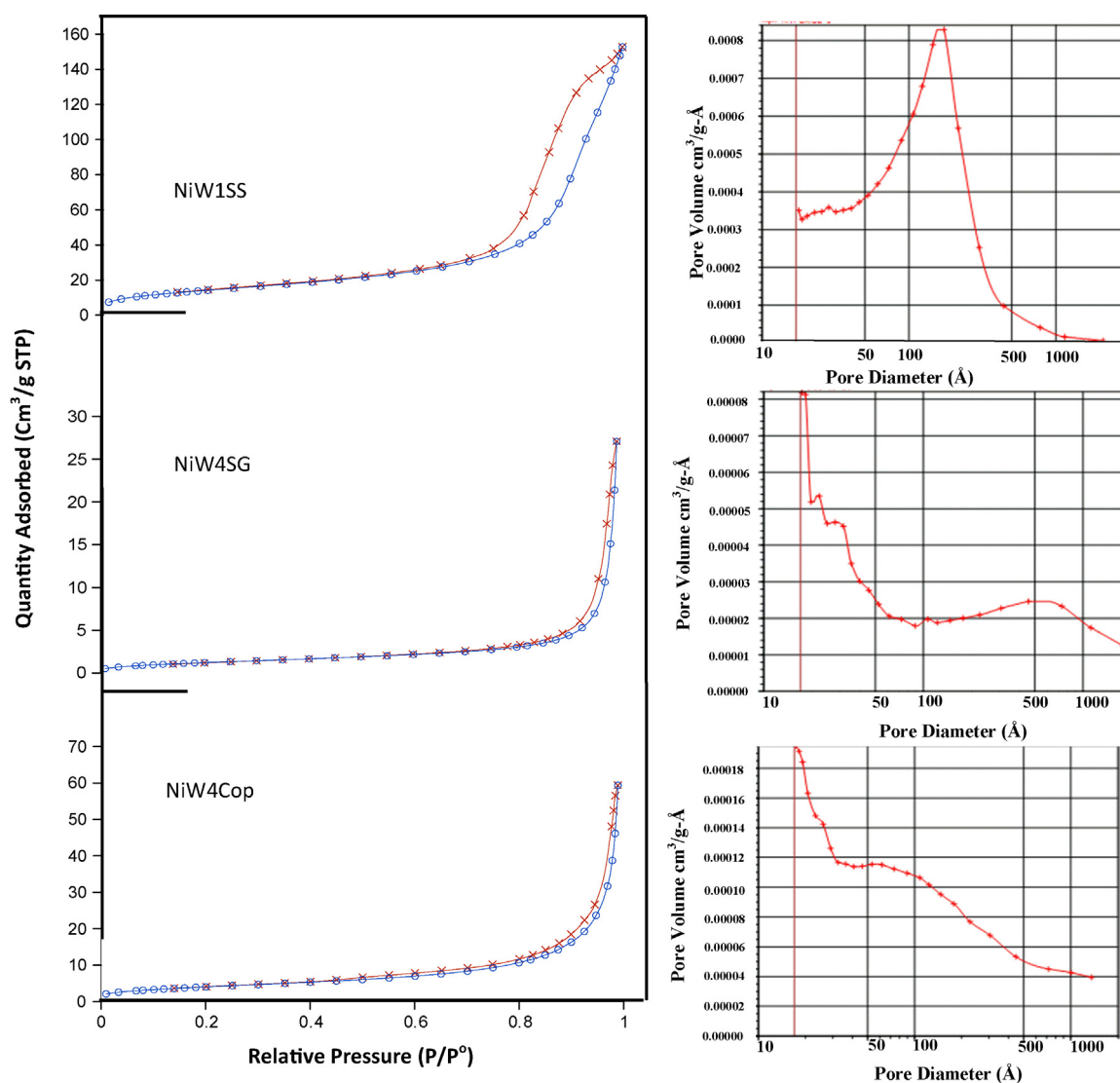


Fig. 3. Adsorption–desorption isotherms and pore size distribution of NiW_{1SS}, NiW_{4SG} and NiW_{4COP}.

NiW_{4SG} indicates that it's composed of mesopores with quite narrow distributions centred at 20, 30 and 120 Å, as well as macropores centred at 600 Å, seen as a broad band. Such macropores explain the reason for the marked decrease in S_{BET} of this particular sample. In addition, deposition of residual amounts of non-decomposed triblock copolymer moieties in the pores of NiW_{4SG} affects the pore volume [0.0164 cm³/g for NiW_{4SG} vs. 0.0491 cm³/g for NiW_{4COP} and 0.2061 cm³/g for NiW_{1SS} (Table 1)] that by in turn affects the surface area value. On the contrary, NiW_{4COP} showed a bimodal distribution centred at 25 Å; as a shoulder, together with a broad one centred at 60 Å. The shape of the nitrogen adsorption–desorption isotherm is strongly influenced by the W/Ni atomic ratio, e.g. in the 1:1 ratio; as in NiW_{1SS}, mesopores were only existed with larger hysteresis loop than NiW_{4COP} synthesized using the same template (PEG) but with varied atomic ratio (W/Ni = 4). This let us presume that in the NiW_{1SS} sample, PEG 2000 has been well assembled in a facile way to form large ordered mesoporous NiWO₄ whereas this ordering is somehow narrowed when the atomic ratio raised to 4 in NiW_{4COP}. This probably due to the absence of WO₃ moieties in the NiW_{1SS} sample as depicted from XRD results unlike the case in the other samples. NiW_{4SG} revealed a combination of both meso- and macropores whereas NiW_{4COP} displayed only a lower margin of mesopores. NiW_{4SG} and NiW_{4COP} samples presented

similar adsorption–desorption isotherm except that the desorption step in the former was at $P/P^0 = 0.85$ where it was at 0.55 for the later reflecting that varying the polymeric template from triblock to polyethylene glycol affects the ink-bottle type of pores ($P/P^0 > 0.5$) [27,28] produced for the shaped NiWO₄. Narrowing parts of the mesoporous channels and creating ink-bottle like sections can be recognized in the NiW_{4SG} sample and as a result a trimodal distribution is revealed at 20, 30 and 120 Å upon employing the triblock copolymer template. Deposition of WO₃ and/or carbons in the pore structure of the formed NiWO₄ phase can produce such small distributions, as has been affirmed from HRTEM results of this sample that showed the close contact between both phases (WO₃/NiWO₄).

3.3. Optical and vibrational properties

The optical properties of the samples are characterized by UV–vis spectroscopy (Fig. 4). Four absorption bands at 329, 382, 455_{sh} and 739 nm are observed in NiW_{1SS}. It has been reported that crystalline NiWO₄ exhibits an adsorption band at 450 nm as well as at 342 nm [28] whereas WO₃ displays an absorption band at 718 nm [29]. Accordingly, by matching, the absorption band positioned at 382 nm constitutes with those depicted at 329 and 455_{sh} nm the formation of NiWO₄ since neither WO₃ nor NiO has

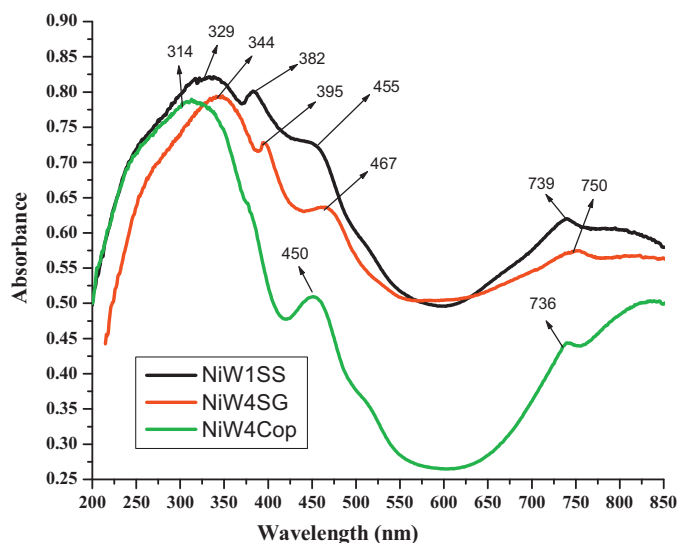


Fig. 4. UV-vis DRS spectra of NiW_{1SS}, NiW_{4SG} and NiW_{4Cop}.

absorption bands around the wavelength at 382 nm. Assigning the band at 739 nm into WO₃ matching that at 718 nm [30] was not in agreement with XRD data indicating that the formed WO₃ phase in NiW_{1SS} was in amorphous state, rather than in crystalline one. Similarly, the NiW_{4Cop} sample indicates similar bands as shown for NiW_{1SS} but at lower wavelengths (314, 450 and 736 nm) together with vanishing that at 382 nm. The NiW_{4SG} sample indicates the same bands as in NiW_{1SS} except that significant enhancement to visible light bands was revealed. The bands at 329, 382 and 455 nm ascribed to NiWO₄ in NiW_{1SS} are shifted into 344, 395 and 467 nm, respectively in NiW_{4SG}. This shift to higher wavelengths is probably related to the dispersed particles and to the difference in particles size of NiW_{4SG} compared to NiW_{1SS}, [31] as illustrated in XRD and TEM investigations. Meanwhile, UV-vis results revealed that NiWO₄ nano-particles have good light absorption properties not only in the UV region but also in the visible light ones. Shifting the WO₃ band at 739 nm in NiW_{1SS} into 750 nm in NiW_{4SG} was in conformity with the conclusion obtained from XRD data stating that NiW_{4SG} owns the highest crystallized WO₃ phase between all samples. This declares that UV-vis spectroscopy is rather sensitive in detecting the existence of any crystalline WO₃ phase.

In order to determine E_g , we have analyzed the measured absorption spectra of the studied tungstates, by calculating the absorption edge as depicted in Fig. 5. The values of optical transition obtained by extrapolating the straight line portion to energy axis at zero absorption coefficients give the direct optical band gaps. In particular, we found that E_g decreases in the following sequence NiW_{4Cop} > NiW_{4SG} > NiW_{1SS}. For NiW_{4SG}, the determined E_g (2.53 eV) agreed well with the value reported in the literature [32]. In case of NiW_{1SS}, the measured E_g is 2.23 eV. This suggested that the band-gap energy of NiWO₄ synthesized by the simple addition via employing PEG-2000 was much lower than the previously accepted value (2.56 eV) [33] whereas that calculated for NiW_{4Cop} was 2.92 eV, indicating the capability of the former for capturing visible light, comparatively. In wolframite-structured tungstates the upper part of the valence band consists mainly of the O²⁻ 2p states, and the conduction band is dominated by the W⁶⁺ 5d states, in a similar way as it occurs in WO₃ [34]. Including the transition metal Ni in tungsten to form tungstate invokes the O²⁻ 2p states and the W⁶⁺ 5d to hybridize with d electrons of the Ni²⁺ cation. The smaller band-gap of the samples could be caused by the larger contribution of the metal states to the valence and conduction bands [35]. The UV-vis spectra allow for discrimination between mildly distorted isolated WO₄/WO₆ (E_g > 4.4 eV) and polymeric structures (E_g < 4.0 eV) [29]. Decreasing E_g values than 4 eV in our synthesized materials invokes that they are mainly tungstate compounds (NiWO₄). The shift of the absorption edge in NiW_{1SS} to E_g of 2.23 eV

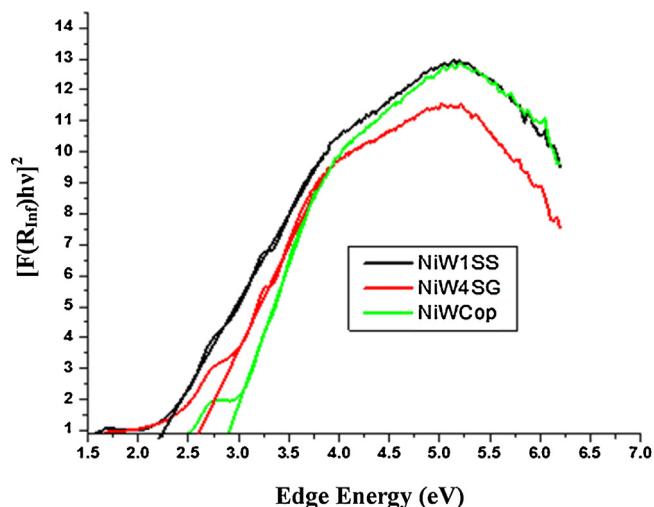


Fig. 5. Energy gap (E_g) values of NiW_{1SS}, NiW_{4SG} and NiW_{4Cop}.

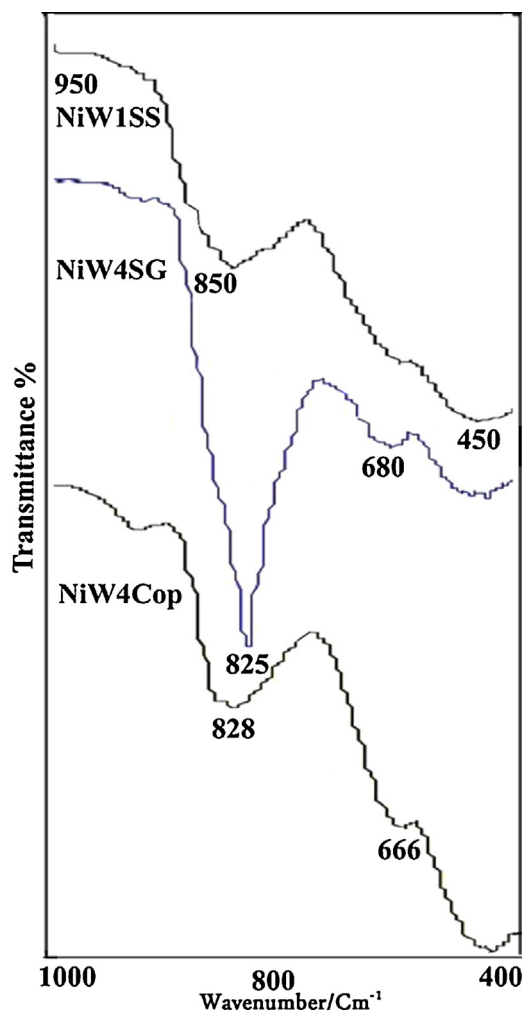


Fig. 6. FTIR spectra of NiW_{1SS}, NiW_{4SG} and NiW_{4Cop}.

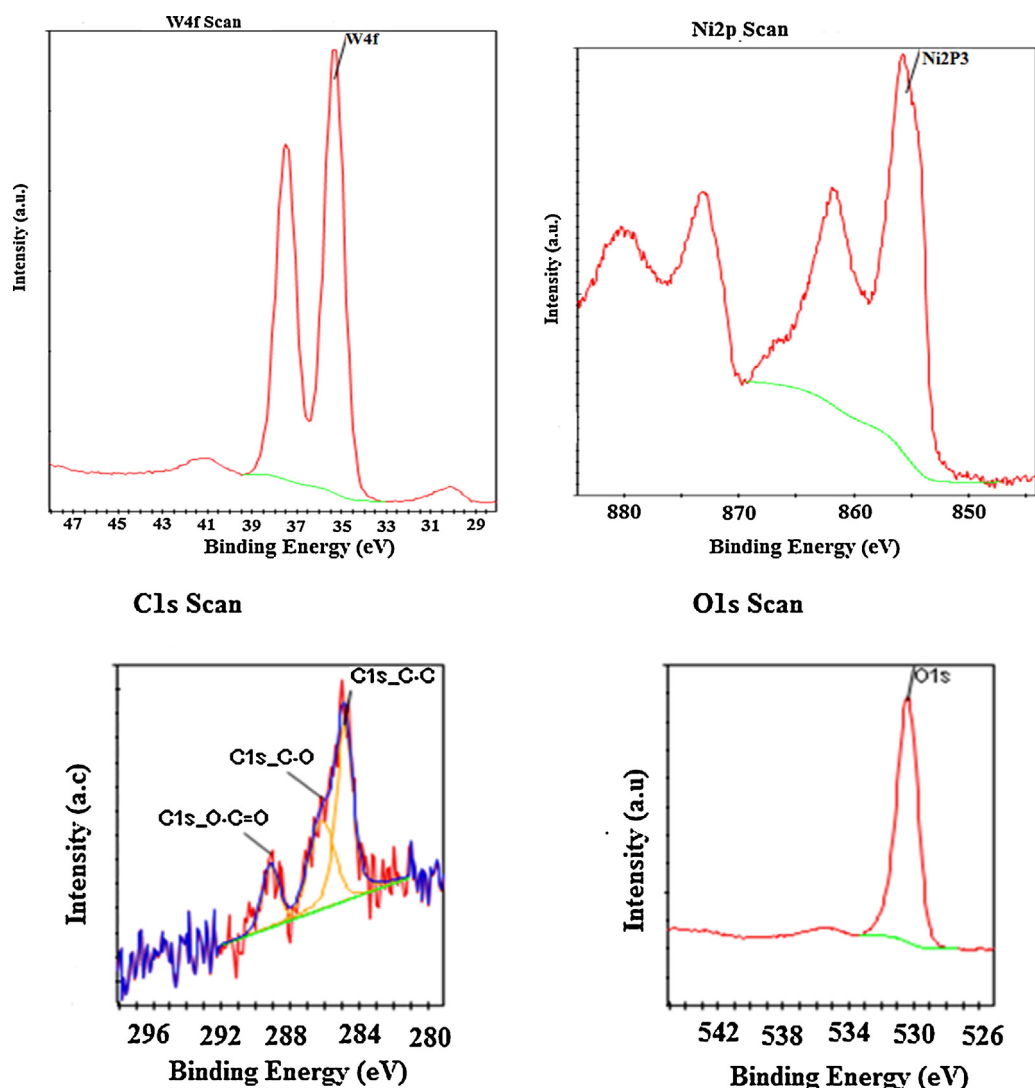


Fig. 7. X-ray photoelectron spectra of W4f, Ni2p, C1s and O1s transitions of the NiW_{4SG} material calcined at 400 °C.

compared to 2.56 and 2.92 eV for NiW_{4SG} and NiW_{4COP} respectively, is correlated to the increase in particle size of the former comparatively as depicted from XRD and TEM results, reflecting that narrowing the energy gap is due to quantum size effects. The shift of the absorption edge in nano NiW_{4COP} to higher energies compared to NiW_{4SG} is also devoted to the increase in particles size of the former (Table 1) comparatively. It is well known that, as a consequence of quantum confinement of the photogenerated electron–hole pairs, the UV–vis absorption spectra of semiconductor nanoparticles are size dependent [36]. Particularly, the wavelength at the maximum exciton absorption (λ_{\max}) decreases because of the decrease of the nanoparticles size [37]. This was not affirmed for the NiW_{4COP} sample that expected to own the lowest optical band gap since it showed the lowest maximum absorption between all samples. This was due to the evolution of some other phases beside NiWO₄ such as low crystalline WO₃ nanoparticles that causes widening of the energy gap. This points out that WO₃ nanoparticles; of decreased particle size, and in close proximity to NiWO₄ in NiW_{4COP} could cause an increase in band gap energy due to quantum confinement effect [38] unlike the case in NiW_{4SG} in which well crystallized WO₃ decreased the E_g of NiWO₄.

The IR spectra of calcined samples are shown in Fig. 6. In the IR spectrum of the NiW_{1SS} sample, broad bands at 950, 850, 666 and 450 cm^{−1} are depicted to confirm the NiWO₄ formation where the

band at 950 cm^{−1} is ascribed to the stretching modes of the W=O terminal bond present in each octahedron of WO₃ [39]. Since XRD results of the sample indicated the presence of negligible amounts of low crystalline WO₃ hence this band is likely due to the highly dispersed WO₃ species. This may also indicate that the material has a high long-range disorder with some short-range order. This was in conformity with the assignment of the 739 nm band depicted for the same sample when using UV–vis spectroscopy technique. The absence of bands at 805 and 750 cm^{−1} due to stretching vibrations of bridging W–O–W bonds [40] confirms the assignment concerning the NiWO₄ formation. Additionally, the observed band at 450 cm^{−1} confirms the stretching vibrations of the NiO₆ polyhedra building NiO [41,42], validating the formation of NiWO₄ structure. In the NiW_{4COP} sample, the band at 950 cm^{−1} is appeared, in conformity with XRD results, together with broad bands at 828, 450 and 666_{sh} cm^{−1}. The vibrational spectrum of the NiW_{4SG} sample presented typical bands as in NiW_{4COP} at 825, 680 and 450 cm^{−1} except that at 666 cm^{−1} in the later is shifted to 680 cm^{−1} in the former and became broader. The broadness of the 680 cm^{−1} band explains that NiWO₄ in NiW_{4SG} was not completely pure probably due to its association with the crystalline WO₃ phase [43,44]. An evidence of the formation of the WO₃ phase in the NiWO_{4SG} sample was also depicted by the broad band at 950 cm^{−1}, in conformity with XRD and DRS investigations. It is interesting reporting that IR spectra

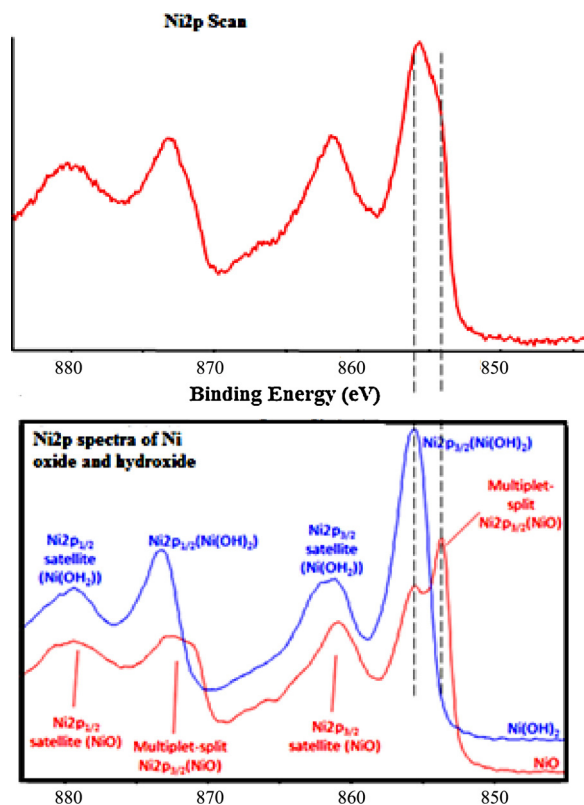


Fig. 8. Peak fitted Ni2p signals to NiO and Ni(OH)₂ in NiW_{4SG} sample calcined at 400 °C.

of our synthesized samples showed bands in the 1338–1775 cm^{−1} region due to residual organics as a result of the incomplete decomposition of the templates (see supporting information) and this was in conformity with TGA data.

3.4. XPS analysis

Fig. 7 shows the spectra of Ni2p_{3/2} and W4f_{7/2} of the NiW_{4SG} catalyst annealed at 400 °C. The asymmetric Ni2p_{3/2} XPS main peak seen at 855.4 eV shows one additional structure at the high BE side, named satellite peak at 862 eV. This is suggestive of multiple oxidation states of Ni. The Ni2p spectrum is compared to two reference spectra from NiO and Ni(OH)₂ (Fig. 8). The NiO reference spectrum has a peak at about 854 eV, which is seen in the NiW_{4SG} sample as a shoulder [45]. It has also a sharper satellite line at about 860 eV, resemble that in the same spectrum, along with a shoulder at ~866 eV. The Ni(OH)₂ reference spectrum has a broad peak at 855.5 eV, which is close to the maximum of the NiW_{4SG} sample. The broader satellite at 860 eV does not resemble that of NiW_{4SG} in a firm way, so if Ni(OH)₂ is present, it is not the dominant component. Based on these reference data, the reasonable interpretation of NiW_{4SG} is most likely being predominantly NiO, with an additional state that could be Ni(OH)₂, or something that causes a similar shift in the Ni2p peak. This could account for a different local environment of the Ni atoms in the bulk structure, influencing the Ni–O interaction. The shift of Ni2p to higher BE compared with Ni rich samples [46] is very much related to the presence of tungsten atoms in the structure of the Ni–W–O catalyst nearby the surface of the material, as can be seen in NiW_{1SS} (856.2 eV, Table 2). Exceeding the BE of the latter band in NiW_{1SS} to higher values is probably due to the presence of Ni³⁺ provoking its existence on the synthesis method used [47].

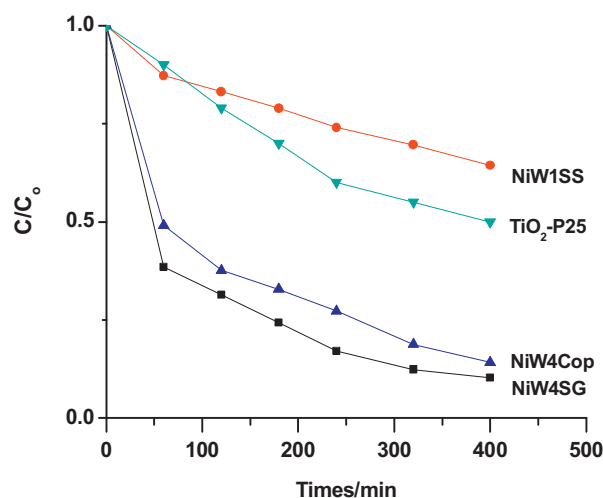


Fig. 9. Change in the relative dye concentration vs. time for the synthesized NiWO₄ photocatalysts (reaction conditions: 350 ml of 20 ppm MB, 200 mg catalyst, 750 rpm).

Indeed, IR and XRD results confirmed the presence of NiWO₄. In addition, the BE of the Ni2p_{3/2} XPS secondary peaks clearly change with increasing tungsten content in the sample (Table 2). This could account for a different local environment of the Ni atoms in the bulk structure [48]. Fig. 7 also shows that the W4f spectra in our sample consist of well-resolved spin orbit split doublet peaks corresponding to W4f_{7/2} at 35.6 eV, and W4f_{5/2} at 37.5 eV, close to the binding energy for W4f_{7/2} in NiWO₄ [16,18], i.e. resembling that of W⁶⁺. A shift to lower BE in the W4f_{7/2} main peak in the sequence NiW_{1SS} > NiW_{4SG} > NiW_{4Cop}, compared with that of bulk WO₃ [32], with increasing W content, is clearly observed (Table 2). This could be related to the presence of Ni atoms in the local environment of W⁶⁺ species [23]. XPS data seen in Table 2 confirmed the presence of non-reacted amounts of NiO in NiW_{4SG} and NiW_{4Cop} samples synthesized at a nominal molar ratio of 4 (W/Ni). The ratio between Ni, W, and O in NiW_{4SG} and NiW_{4Cop} samples is not close to the stoichiometric of 4 for W/Ni, unlike that depicted from EDX elemental compositions, proposing the non-homogeneity of the sample.

The C 1s spectrum has been fitted with three components; as shown in Fig. 7, to show chemical states due to hydrocarbon (C–C) and alcohol, ester or carboxylate (C–O, O–C=O). This is not consistent with typical adventitious contamination used to be because of their high amounts, thus it probably came from the non-complete decomposition of the triblock copolymer template as evidenced by the TG technique (not shown). The O 1s peak seen at 530.4 eV indicated the presence of nanosized NiWO₄. It is expected that a local structure relaxation in nano-NiWO₄ will slightly decrease the O 1s binding energy compared to that of crystalline NiWO₄. Moreover the phases with larger O 1s binding energies, such as Ni(OH)₂ could contribute to the larger shift towards lower binding energies [49]. This can be related to the appearance of a nickel oxide phase in which oxygen atoms have lower binding energy [50].

3.5. Photocatalytic degradation

After equilibration of the dye–photocatalyst suspension in the dark, the photo-degradation of the methylene blue (MB) dye was found to depend on the nature of the synthesized NiWO₄ catalysts: 30.0% for NiW_{1SS}, 92.5% for NiW_{4SG} and 81% for NiW_{4Cop}. The decolourization behaviour of MB on NiWO₄ photocatalysts is shown in Fig. 9. It is important to notify that the contact time prior to irradiation was 30 min for all samples and it was 400 min

Table 2XPS results including surface composition (at %) for synthesized NiW_{1SS}, NiW_{4COP} and NiW_{4SG} catalysts.

Sample	Ni2p3/2 main peak (eV)	Ni2p3/2 secondary peak (eV)	W4f7/2 main peak (eV)	W4f7/2 secondary peak (eV)	Ni% from Ni2p	W% from W4f	O% from O1s
NiW _{1SS}	856.2	861	35.56	37.43	8	9	35
NiW _{4SG}	855.4	862.2	35.33	37.5	8	19	36
NiW _{4COP}	855.3	863	35.21	37.35	6	17	41

during the MB photo-oxidation reaction. This is very important to reveal the effect of surface area and particle size of the samples while performing the reaction. It is observed that NiW_{4SG} is the most active while NiW_{1SS} is the least active photocatalyst for the degradation of MB even when compared with P25 TiO₂ that presented activity composed of 46%. From the plot (not shown) of the decolorization rate vs. the irradiation time, straight lines can be fitted in the first part of the plots, estimating apparent first order kinetic constants of 0.017, 0.012 and 0.003 min⁻¹ for NiW_{4SG}, NiW_{4COP} and NiW_{1SS}, respectively. It can be seen that the surface area of the materials has an opposite trend with respect to that revealed by the amount of MB degraded on the photocatalysts since NiW_{4SG} that exhibited the lowest surface area value presented the highest activity. Accordingly, calculated turn over frequency expressed per unit total area of catalysts was 0.18×10^{-3} , 0.57×10^{-4} and 0.17×10^{-4} mmol m⁻² min⁻¹ for NiW_{4SG}, NiW_{4COP} and NiW_{1SS}, respectively. The low activity of NiW_{1SS} (having band gap of 2.23 eV) towards the degradation of MB may be related to the inaccessibility of the catalysts to the photons of the wavelength needed to generate oxidizing species since MB in solution acts as a shield for absorbing incoming photons, hindering the direct interaction of photons with the photocatalyst. On the contrary, NiW_{4COP} and NiW_{4SG} those showed higher band gaps encompassing the range from 2.56 to 2.92 eV exhibit lower adsorption comparatively and thus allowed the energy transfer by the excited dye molecules. It is well established [51] that the adsorption in the dark of a substrate on the surface of the semiconductor acts a vital role in its degradation under irradiation. In fact, the amount of the dye adsorbed in the dark provides a rough estimation of the nature and number of available adsorption sites present at the surface of the catalyst. This parameter is not easily evaluated under irradiation since additional adsorption sites may be generated with the possible formation of surface defects [52]. A rather high adsorption of the substrates must be guaranteed in order to efficiently promote their degradation, while the complete surface coverage is often detrimental, as was observed in the case of NiWO₄ in the work of Fornasiero et al. [53]. In this case, the dye acts as a shield, hindering the direct photon absorption leading to an inactive catalyst. In the later work [53], the catalytic activity of NiWO₄ was not evaluated, since the catalyst surface was fully covered by adsorbed MB reaching great values as high as 92% where it gives activity comprised of 10% degradation in case of methyl orange dye. Accordingly, the differences in the photocatalytic activity in our tungstates can be ascribed to exceeding the adsorption on NiW_{1SS} (19.7%) than on NiW_{4SG} and NiW_{4COP} (10.9–11.5%). Thus, we believe that the reactivity on the later catalysts is mainly due to electronic properties rather than adsorption ones. Increasing the adsorption on NiW_{1SS} comparatively could be due to the presence of appreciable amounts of the amorphous WO₃ in conformity with the work of Luo et al. [54]. This let us presume that severe adsorption will inhibit the production of oxidizing species, through water oxidation, irrespective of lowering the E_g of the NiW_{1SS} catalyst; comparatively, and thus prohibits reaching the photons into the surface. In consistence, the comparison of the performance of the Degussa P25 TiO₂ photocatalyst with NiW_{4SG} was significant. This former reference material showed a lower activity ($k=0.0041$ min⁻¹) with respect to the

latter, probably due to a higher percentage of MB adsorption on its surface (24.8%).

However, as mentioned in the results obtained, the synthesized NiW_{4SG} catalyst exhibits an obvious difference in particle morphology. This decisive difference in morphology that correlated with the decrease in particles size (25 nm) together with the noticed close contact between WO₃ and NiWO₄ moieties probably influenced the photocatalytic activity, i.e. the exposed crystal faces and/or the ratios among exposed crystal faces (Table 1) are undeniably have decisive influences in inhibiting the recombination between electrons and holes. Accordingly, the finer particles size of NiW_{4SG}, the shape as well as the crystalline WO₃ species influenced the activity towards MB degradation. The low recombination rate of electrons and holes is also an indispensable reason for exceeding the photocatalytic activity of NiW_{4COP} than that on NiW_{1SS} since the former shows some crystalline WO₃ species [55], which have exceptional chemical and photoelectrochemical stability in aqueous media over a very wide pH range. Accordingly, the enhancement of the photocatalytic activity of NiW_{4SG} and NiW_{4COP} is due to effective charge separation caused by trapping the photogenerated electrons.

A mechanism for the increase in photocatalysis by NiW_{4SG} is shown schematically in Fig. 10. Under UV illumination, electrons (e⁻) are excited from the valence band (VB) to the conduction band (CB) of NiWO₄, creating a hole (h⁺) in the VB. Only a small number of electrons and holes usually participate in photocatalytic reactions resulting in a low reactivity, while the rest are lost due to recombination. WO₃ mainly absorbs in the near ultraviolet and blue regions of the solar spectrum because of its band gap ($E_g = 2.6$ eV to approximately 2.8 eV) [56]. As a basic function, WO₃ has a suitable conduction band potential to allow the transfer of photogenerated electrons to NiWO₄ facilitating effective charge separation as well as hindering recombination. It is easy for electrons to transport from WO₃ to the NiWO₄, because of the close contact and large interface area between them that has been attained via coupling of the WO₃ semiconductor with NiWO₄.

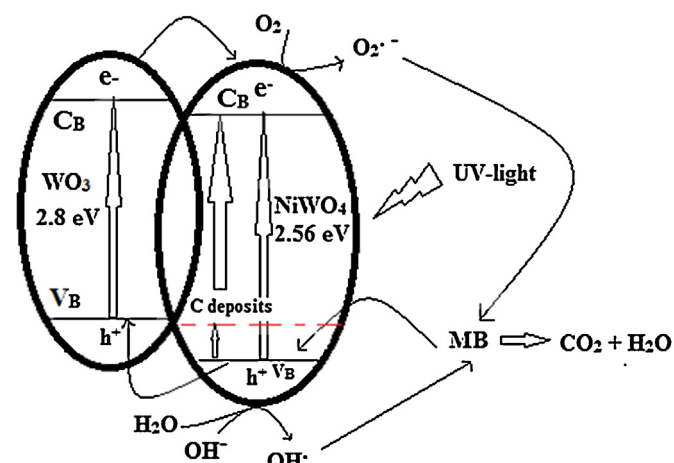


Fig. 10. Scheme for electron–hole separation and transport at UV-light driven NiWO₄(WO₃) photocatalyst interface.

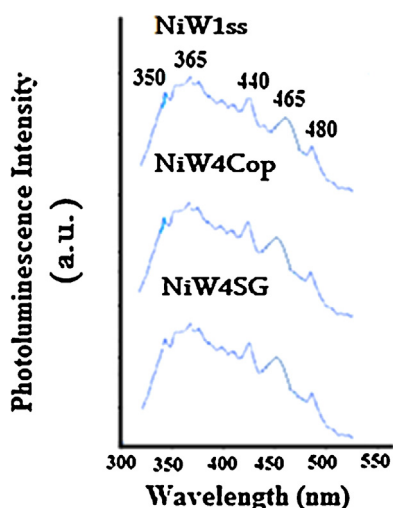


Fig. 11. PL spectra (excitation wavelength of 290 nm) for NiWO₄ nanoparticles synthesized by different methods.

This is rather surprising results given that previous reports suggest that NiWO₄ in its own is either inactive or slightly active in the photocatalytic removal of organics [57,58]. Perceiving such high activity let us presume that residual carbons can act as hole scavenger; as well, to contribute to the apparent activity together with the mentioned parameters discussed above including morphology and the close contact between WO₃ and NiWO₄ species. In concordance, the TGA diagram of NiW_{4SG} (not shown) evidences the presence of residual organic template following annealing at 400 °C. However, the absence of carbons in XRD results confirms that it is likely to be in an amorphous state. This doping by the non-metallic carbon has shown to result in visible-light sensitization of TiO₂ [59,60]. It has been extensively approved that carbon doping would introduce a mid band-gap state close to the TiO₂ VB and extends light absorption to longer wavelength region [61]. Therefore, the synthesized carbon-doped NiW_{4SG} hybrid (Fig. 10) with WO₃ shows a higher UV light photocatalytic activity towards MB degradation.

In conformity, photoluminescence emissions spectra arise from the recombination of free carriers are carried out for all synthesized catalysts, as shown in Fig. 11. The emissions for all synthesized NiWO₄ nano-particles were at wavelength range of 300–500 nm. The observed patterns were similar to other wolframite compounds; Originated from the WO₆⁶⁻ anion along with some defects in the crystal structure [62]. The emission bands at 350 and 365 nm come from the band gap transition, where the small doublet peaks appear at 400 and 410 are due to either the quantum size [63] and/or to the interference between the luminescence band of the WO₆ groups and the absorption band of the NiO₆ groups [64]. The obvious emission peaks of 440, 465 and 480 nm are related to the intensive transition from the ground state ³A_{2g} to the excited state ³T₁ of Ni²⁺ (3d⁸) ions [64] in distorted octahedral coordination [65] or due to recombination of e–h pairs localized at oxygen-atom-deficient tungstate ions [66]. The PL emission spectra of the synthesized wolframite NiWO₄ nanoparticles show similar peak positions with varied PL intensities. The PL intensity of the NiW_{1SS} sample was significantly higher than those of NiW_{4COP} and NiW_{4SG}. The reason lies in the fact that the PL emission mainly results from the recombination of photo-excited electrons and holes, and then a lower PL intensity might indicate a lower recombination rate of those electrons and holes under light irradiation [67]. Accordingly, the deposition of WO₃ on NiWO₄ forming hybrid structure in both NiW_{4COP} and NiW_{4SG} nanoparticles reduces PL emission intensity significantly, and thus favours the enhancement

of their photodegradation properties comparatively based on avoiding electron–holes recombination in the WO₃/NiWO₄ heterojunction.

4. Conclusion

It has been shown that the synthesis techniques including simple salt addition, co-precipitation and sol–gel as well as the molar ratio of W/Ni together with the template type including PEG and triblock copolymer affected greatly the characteristics of the produced NiWO₄ materials. Of particular interest the existence of WO₃ phase, at a molar ratio (W/Ni) of 4, either in amorphous or in well crystalline state beside NiWO₄, affects greatly the surface, electronic and morphological properties of the produced catalysts. The NiW_{1SS} material, synthesized at molar ratio of 1 and only exposes NiWO₄, indicated monomodal mesoporous distribution as well as the lowest *E_g* (2.23 eV) between all synthesized tungstates. This elaborates the effect of the PEG template in synthesizing mesoporous structure of nanoplate shape, of average size of 34 nm, and high surface area value. At a nominal molar ratio (W/Ni) of 4, the NiW_{4COP} and NiW_{4SG} samples those synthesized, respectively using PEG and triblock copolymer templates presented different properties. In particular, the latter material presented macropores and mesopores of nanoflake shape, average sizes of 25 nm, and well crystallized WO₃ in close contact with NiWO₄, and thus exhibited *E_g* value of 2.56 eV. The former indicated amorphous WO₃ that widen the *E_g* of NiWO₄ to 2.92 eV. Despite its large band gap comparatively, NiW_{4SG} presented the highest photocatalytic activity (92.5%); ever reached for the first time, among all synthesized nickel tungstates studied so far in the degradation of MB. The higher activity of NiW_{4SG} for the degradation of MB was correlated to the increase in the lifetime of the electron–hole pair facilitated by the presence of WO₃ crystallites; as confirmed by PL spectroscopy, due to the strong heterojunction with NiWO₄ and to decreasing the crystallites size. This study proved that they are a new class of inspired photocatalysts that are worthy to be further studied and can be a valuable addition in photocatalyst collection in future.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.12.001>.

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